PHOTOELECTRON SPECTROMETER FOR HIGH RESOLUTION ANGULAR RESOLVED STUDIES

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We report on a new electron spectrometer system designed for use on storage ring light sources. The system features a large (76 cm diameter × 92 cm long) triply magnetically shielded vacuum chamber and two 10.2 cm mean radius hemispherical electron energy analyzers. One of the analyzers is fixed and the other is rotatable through about 150°. The chamber is pumped by a cryopump and a turbomolecular pump combination so as to enable experiments with a variety of gases under different conditions. The light detection includes both a direct beam monitor and polarization analyzer. The electron detection is accomplished with either a continuous channel electron multiplier or with multichannel arrays used as area detectors.

1. Introduction

Photoelectron spectroscopy using variable wavelength capability has proven to be an extremely valuable tool in the study of atomic and molecular photoionization. Recently, particular applications of synchrotron radiation have been reviewed extensively in the literature [1–6].

The variable wavelength capability of synchrotron light sources combined with appropriate monochromators has enabled a new generation of instruments to be built which exploit this feature. The first such instrument at NBS utilized a rotatable 5 cm mean radius hemispherical electron energy analyzer coupled with a high flux normal incidence monochromator [7,8]. This instrument has performed well over the past several years resulting in studies on a number of atomic and small molecular systems [9]. This work has studied the effects of autoionization and shape resonances upon photoelectron branching ratios and asymmetry parameters. Striking non-Franck–Condon transition amplitudes have been observed in a number of molecules in the wavelength regions of resonance phenomena.

The energy resolution of the 5 cm mean radius system was typically 110 meV with a photon band pass of about 15 meV. With a combined resolution of about 120 meV, vibrational structure in diatomic and small polyatomic molecules could be separated. With larger molecules (i.e. such as C_2H_2, CH_3CN etc.) the vibrational spacing can be significantly less than 100 meV. For

example, in acetylene some important vibrational modes of the ion have energies of 36 meV and 86 meV. The 5 cm mean radius instrument cannot easily resolve these features while maintaining sufficient acceptance aperture and transmission to economically gather data.

The scientific importance in measuring these non-Franck–Condon effects accurately along with the desire to obtain better magnetic shielding, higher sample throughput and the adaptation to area detector technology have prompted us to design an entirely new instrument which we herein report upon.

2. Vacuum system

The chamber is a 76 cm diameter, 92 cm long stainless steel vacuum chamber. Fig. 1 shows a cross section of the chamber through the midplane. The chamber has eight 25 cm diameter metal seal input flanges which can be used to introduce electrical and mechanical facilities as well as to provide for pumping.

The system is pumped with a 500 l/s turbomolecular pump for use in gas load situations and a 2000 l/s closed cycle helium cryopump for use with condensible gases and maintaining static vacuum requirements. Liquid nitrogen cooled absorption cryopumps are used for initial evacuation to minimize the possibility of hydrocarbon contamination. The system was designed to conform with ultrahigh vacuum considerations, and, as such, features all metal seals on the ports although
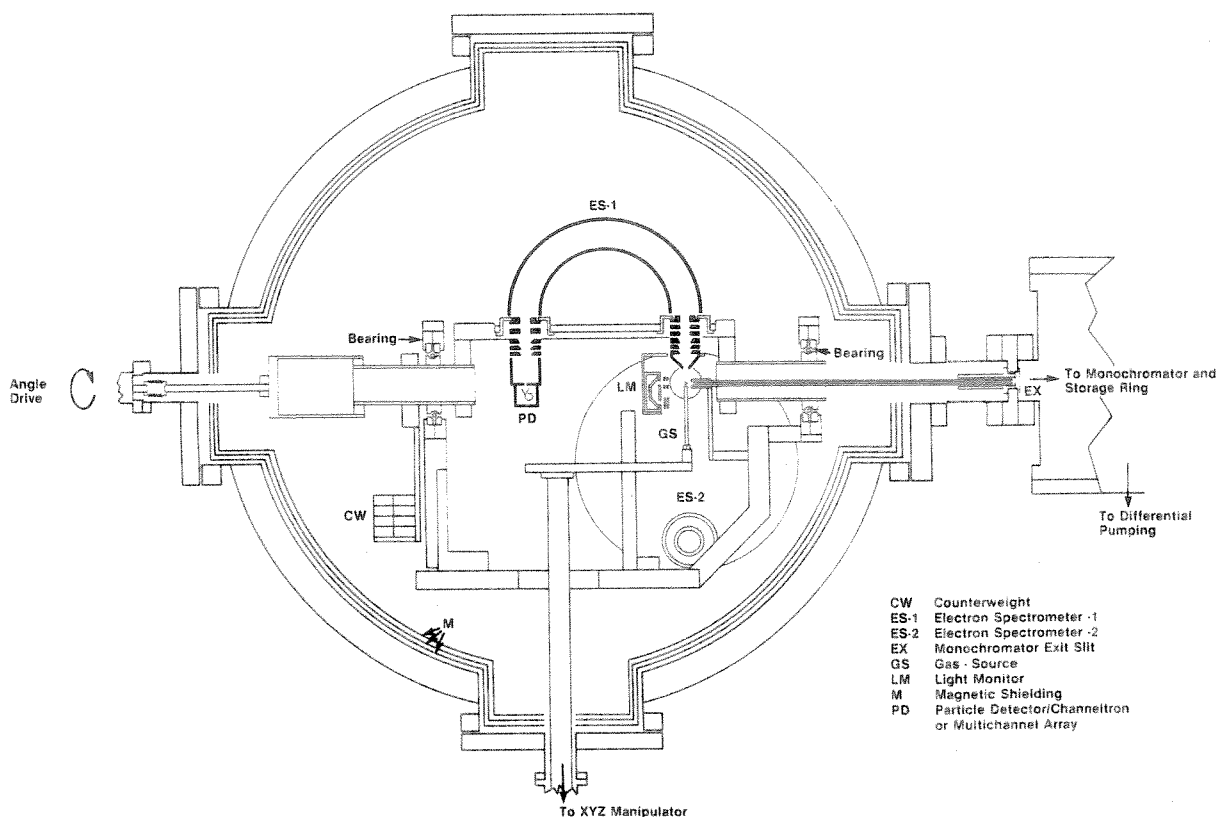
Fig. 1. This figure gives a schematic representation of the electron spectrometer system. The major components of the apparatus are labeled and described in the figure and some details are omitted to help clarity.

the large end flanges are routinely sealed with appropriate elastomers. The system achieves pressures of $\sim 10^{-8}$ Torr without bakeout.

The magnetic shielding is supplied by three layers of high magnetic permeability alloy. Adjacent layers are separated by aluminum spacers with all end caps fastened into place with nuts and bolts. This ensures isolation between the layers and close magnetic coupling between the mating pieces. While in the earth's field, the residual field in the experimentally important volume is on the order of 500 μG. It is expected that when the apparatus is located in the region of the magnet of the SURF-II storage ring the residual internal field will not be significantly different. Care has been taken in selecting components and materials that are situated inside the shielded volume so as to minimize the degradation of the effectiveness of the shielding.

3. Photoelectron spectrometer system

The system is designed to operate in a configuration with either one or two electron spectrometers with the

normal configuration being utilization of two electron spectrometers. One of the spectrometers is rotatable with a rotation axis along the light propagation direction. The result is that when the electron intensity is measured with respect to the principal axis of polarization, the asymmetry parameter can be deduced. The differential cross section can be written:

$$\frac{\mathrm{d}\sigma_v}{\mathrm{d}\Omega} = \frac{\sigma_v}{4\pi}\left(1 + \frac{\beta_v}{4}\left(3P\cos 2\theta + 1\right)\right),$$

where, β_v = asymmetry parameter for vibrational state v, σ_v = total cross section for transition to vibrational state v, P = polarization of the light with the horizontal component being the major axis. θ = angle of ejection of photoelectrons with respect to the horizontal direction. The number of electrons ejected per unit light flux per unit solid angle, $(\mathrm{d}N_v/\mathrm{d}\Omega)$ is proportional to the differential cross section, hence we can write:

$$\frac{\mathrm{d}N_v}{\mathrm{d}\Omega} = N_v\left(1 + \frac{\beta_v}{4}\left(3P\cos 2\theta + 1\right)\right).$$

Measurement of P, θ and the number of electrons as a function of θ enables a determination of β_v and N_v. N_v when normalized over the appropriate number of possi-

ble channels is the branching ratio for the particular transition. The measurement of P is accomplished with a triple reflection polarizer based upon the considerations of Horton et al. [10]. The angles used here were 67.5°, 45° and 61.5° rather than those used by Horton et al. The value of the polarization ratio was recalculated from their values of the optical constants of gold. These values are used for subsequent calculation of P. (It should be noted that the small change in angles caused only minor changes in the polarization ratio.)

The incoming light flux is monitored by a 90% transparent tungsten photocathode on the input aperture of the polarization monitor. After three reflections the light is intercepted by a second tungsten photodiode. The ratios of these two photodiode signals at 0° and 90° with respect to the major polarization axis determine the polarization.

A second polarization and intensity monitor resides in the differential pumping chamber of the monochromator. This device monitors the light before it passes through the exit slit of the monochromator and provides a useful check on the other determination even though it measures light intensity over an extended spectral range about the selected wavelength.

The electron analyzer is an enlarged version of our previous instrument [7] and maintains the same electron lens system. The lens system is based upon the design parameters suggested by Harting and Read [11] for a three element zoom lens. The same lens is used on the exit side of the hemispheres to refocus the electrons on the channeltron. There are no entrance or exit apertures in the plane of the hemisphere and therefore the aperture in the entrance cone determines the basic resolution. This cone aperture and an aperture in front of the channeltron are changeable for control of physical constraints on the resolution. The resolution obtainable while yet maintaining good signal is on the order of 20 meV. This figure is arrived at by considering the relationship between resolution and signal and the difference in the experimental configuration with respect to our present apparatus. This resolution will allow for detailed studies of non-Franck–Condon effects in small polyatomic molecules.

The electrical aspects of the electron spectrometer are maintained much as in the previously described apparatus [7]. Briefly, the fixed voltages are controlled by highly regulated conventional power supplies and the variable voltages are under computer control. A 16 bit digital to analog converter (DAC) with a basic increment of 0.0005 V will control the ramping and offset voltages. The variable focus voltages are controlled by isolated power sources run by the computer. The computer (LSI-11) resides in a CAMAC crate and also controls the grating drive, angular position, light detection system, electron counting system and other experimental chores. The data are recorded both magnetically on floppy disks and on hard copy. Both analyzers are ramped off the 16 bit DAC but have their own separately controlled power supplies for lens voltages. The two identical instruments will allow a determination of the branching ratios and asymmetry parameters without rotation, i.e. the electron intensity at two angles can be measured simultaneously. The device can be calibrated by reference to a gas with a known cross section and asymmetry parameter [12]. The calibration features for the two instruments are incorporated into a computer program that analyzes and reduces the data.

Area detectors have been purchased and will be integrated into the experiment as time and resources permit. Basically the devices will replace the exit lens assembly and channeltron and provide a 2-dimensional sensitive array which can be suitably calibrated on an electron energy scale. This is performed by converting a pulse height to electron energy in computer software. The software overhead for the computer will increase significantly and call for revision of our hardware and operating mode.

The gas inlet system is mounted on an XYZ manipulator for external alignment of the gas jet to optimize signal intensity and resolution. Exit nozzles of the system are interchangeable and provide both effusive beams and supersonic jets by use of pinhole apertures of diameter 7–50 μm. The positioning of the supersonic source is of particular importance and necessitates the positioning capability of this inlet system. With this and considerably enhanced pumping we expect a significant improvement in basic sensitivity of the instrument as compared to our present 5 cm radius single analyzer system.

4. Data reduction

The same LSI-II computer that is used for automation is used for the data reduction. The basic data consist of electron counts as a function of ramp voltage. The ramp voltage is converted, using known quantities, to electron kinetic energy. The electron counts are then normalized for correction factors that depend upon kinetic energy, such as the transmission functions of the instruments and any angular correction factors. Upon obtaining a suitably normalized set of data the photoelectron spectra are fitted to a Guassian basis set using spectroscopic values for vibrational energy spacings, and treating peak height, peak width and overall position as free parameters. The areas of the respective peaks are used to infer the values of the branching ratios and asymmetry parameters using the equation developed earlier. The calculated curve and normalized data are plotted to aid in the evaluation of the quality of fit. In addition, this fitting program outputs statistical parameters which can be used to estimate accuracy.

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